

HYDROGEN-OXYGEN ELECTROLYTIC REGENERATIVE FUEL CELLS

Prepared for
National Aeronautics and Space Administration
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio
Attention: D. G. Soltis

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Prepared by

Martin B. Klein
Martin B. Klein
Eugene F. Fiedler
NAS 3-2781
u
Optical
M 7-11-65

Approved by

W. Menetrey
W. Menetrey, Manager
POWER SYSTEMS DIVISION

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1. INTRODUCTION

This report reviews the progress made on a development of a hydrogen oxygen regenerative fuel cell (secondary battery), under NASA Contract 3-2781 during the period April 1 through May 1, 1966. During this period primary emphasis was placed on the testing of single cells with various electrode structures and matrix materials in order to improve cycle life and obtain a better understanding of modes of deterioration that occurred during cycling. Preliminary tests indicate that asbestos matrices are a major factor in performance degradation. Fabrication techniques were established for forming matrix mats using potassium titanate, which appears to be a promising substitute for asbestos.

2. TECHNICAL DISCUSSION

2.1 Single Cell Tests

Nineteen single cell tests were conducted during this period to evaluate the performance of various electrode and matrix structures. Test results and construction variables of these cells are summarized in Table 1. Cells No. 170 and 173 were started in the last report period and consisted of concentration cells of the type described in the 7th Quarterly Report. Cell 170 was a continuous oxygen concentration cell test employing fuel cell type asbestos and gold coated platinized electrodes. The cell was run continuously for a period of 456 hours, at which time the test was discontinued due to excessive overpotentials. During the test period there was a gradual rise in voltage with time as shown in Figure 1. Analysis of a sample of electrolyte squeezed from the mat of the cell revealed a final KOH concentration of 26.25 percent. The electrodes and asbestos mat were relatively clean, with the exception that the porous nickel substrate appeared oxidized, especially on the electrode that was utilized on the oxygen evolution side of the cell.

Cell No. 173 consisted of gold coated platinized electrode and a mat fabricated from three layers of 0.020 inch potassium titanate paper. The cell was put on test as a cycling concentration cell, consisting of 35 minutes at 18 amps. and then reversing the polarity for the next 35 minutes period. Figure 2 shows the mid point voltage of the cell at each direction of current flow as a function of cycles. Figure 3 shows the voltage performance of the cell at various cycles. The test was discontinued after 200 cycles due to high overpotential. As can be seen, there was a gradual rising of voltage with cycling to the end of the test. Note also the difference in voltage as the cell reversed polarity, indicating a difference in the electrode structure and performance of the electrodes within the cell. When the cell was disassembled, the mat appeared extremely dry. A sample of electrolyte could not be obtained for analysis. This test, at the point of conclusion, represented a maximum number of cycles or operating time achieved in a cycling concentration cell.

TABLE 1
SUMMARY OF SINGLE-CELL TESTS

Cell No.	O ₂ Electrode		H ₂ Electrode		Mat Thick (In.)	Mat Dry Wt. (gm)	Electrolyte		Comments	Results
	No.	Catalyst	No.	Catalyst			KOH	Wt. (gm)		
170	64	14 mg Pt/ cm ²	65	14	FC Asb. .060	27.0	40	31.09	Cont. Conc. cell	Run for 456 hrs to 1 V. end pt. Final KOH 26.2%
173	A ₅₂	14 mg Pt/ cm ²	A ₅₁	14 mg Pt/ cm ²	3 layers .020 K.T. Paper	21.5	40	31.0	Cycling concentration times to .95V cell.	Cycled 200 times to end point.
175	-	20 mg Pt/ cm ²	-	20 mg Pt/ cm ²	FC Asb. .060	27.1	40	31.0	O ₂ electrode pasted Pt Black on Nickel Screen	Cycled 10 times Poor perform. Final KOH 29.1%
176	72	"	59	"	4 layers (.020) ACCO I	21.5	40	31.0	Am. Cy. Asb. Matl.	Cycled 4 times low discharge voltage. Final KOH 27.85%
177	Am.Cy.	9 mg Pt/ cm ²	Am.Cy.	9 mg Pt/ cm ²	FC Asb. .060	26.8	40	31.0	Acid washed electrodes.	Cycled 3 times Good perform. Disassembled to replace mat. Final KOH 32.75%
178	A ₆₁	20 mg Pt/ cm ²	A ₁₃₈	20 mg Pt/ cm ²	FC Asb. .060	27.0	40	31.0	Tested as a Primary FC	Ran poor due to water transport diffi-culties.
179	A ₅₈	"	A ₅₇	"	FC Asb. .060	27.0	40	31.0	Tested as a Primary FC Pt. Nickel plaque elect. culties.	Ran poor due to water transport diffi-
180	Am. Cy.	9 mg Pt/ cm ²	Am. Cy.	9 mg Pt/ cm ²	FC Asb. Acid washed	30.0	40	31.0	Electrodes used in Cell 177.	Cycled 45 times Cell exhibited poor eff., fair perform. Final KOH 32%

TABLE 1 (Cont.)
SUMMARY OF SINGLE-CELL TESTS

Cell No.	O ₂ Electrode		H ₂ Electrode		Mat Thick (In.)	Mat Dry Wt. (gm)	Electrolyte		Comments	Results
	No.	Catalyst	No.	Catalyst			KOH	Wt. (gm)		
181	Am.Cy.	9 mg Pt/ cm ²	Am.Cy.	9 mg Pt/ cm ²	3 layers .020 KT paper	-	-	-	New O ₂ electrode Old H ₂ electrode Cycling conc. cell.	Cycled 32 times to 1 V. Showed gradual increase in voltage. Final KOH 32.9%.
182	85	20 mg Pt/ cm ² nickel plaque	86	20 mg Pt/ cm ² nickel plaque	75% KT 25% FC Asb.	20	40	32		Developed internal short on 12th cyc. Good perform. Final KOH 35.2%.
183	Am.Cy.	9 mg Pt/ cm ²	Am.Cy.	9 mg Pt/ cm ²	FC Asb. Acid Washed	30	40.15	31	Cont. conc. cell	Ran 140 hrs. to .95 V. Showed gradual rise in voltage. Final KOH 36.3%.
184	Am.Cy.	"	"	"	"	25	40.15	31	Cont. conc. cell. Electrodes from cell 180	Ran 72 hrs. to 1.2 V. Showed gradual rise in voltage. Final KOH 30.5%.
185	A _u 90	14 mg Pt/ cm ²	A _u 91	14 mg Pt/ cm ²	75% KT 25% FC Asb.	20.0	40	36	-	Still cycling at 150 cycles. Good performance.
186	Am.Cy.	9 mg Pt/ cm ²	Am.Cy.	9 mg Pt/ cm ²	"	20.0	40	31	Cycling conc. cell.	Still cycling at 300 hrs. gradual rise in voltage.
187	Am.Cy.	"	"	"	100% KT	17.5	40.15	31	Old electrodes cont. conc. cell	Ran 27 hours to 1.1 V. Had high initial voltage rose rapidly. Final KOH 35.6%.

TABLE 1 (Cont.)
SUMMARY OF SINGLE-CELL TESTS

Cell No.	O ₂ Electrode Catalyst	H ₂ Electrode No.	Am. Cy.	9 mg Pt/cm ²	Pt/	Mat Thick (In.)	Mat Dry Wt. (gm)	Electrolyte KOH	Electrolyte Wt. (gm)	Comments	Results
188	Am.Cy.	9 mg Pt/cm ²	Am. Cy.	9 mg Pt/cm ²		100% KT	20.0	40	31	Cont. conc. cell. Old electrodes	High initial voltage. Test discontinued.
189	Am.Cy.	"	"	"	"	"	19.9	40	31	-	Short in assembly.
190	Am.Cy.	"	"	"	-	"	19.5	40	31	Cont. conc. cell. Electrodes from 189.	Still on test at 264 hours.
191	115	15	113	15	KT	-	-	-	-	Cont. conc. cell. Felt metal electrodes.	Still on test at 264 hours.

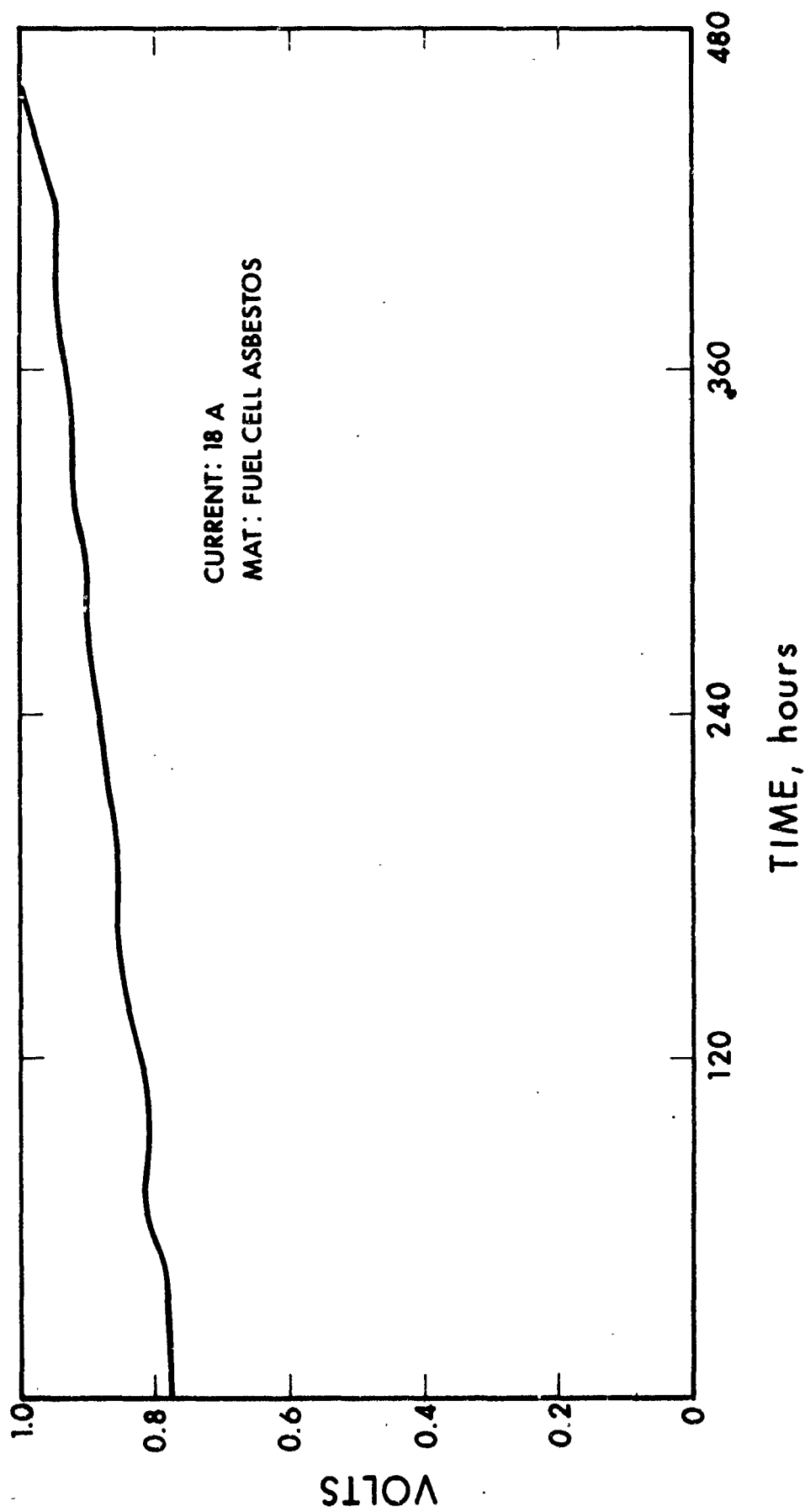


FIG. 1 CONTINUOUS O₂ CONCENTRATION CELL 170

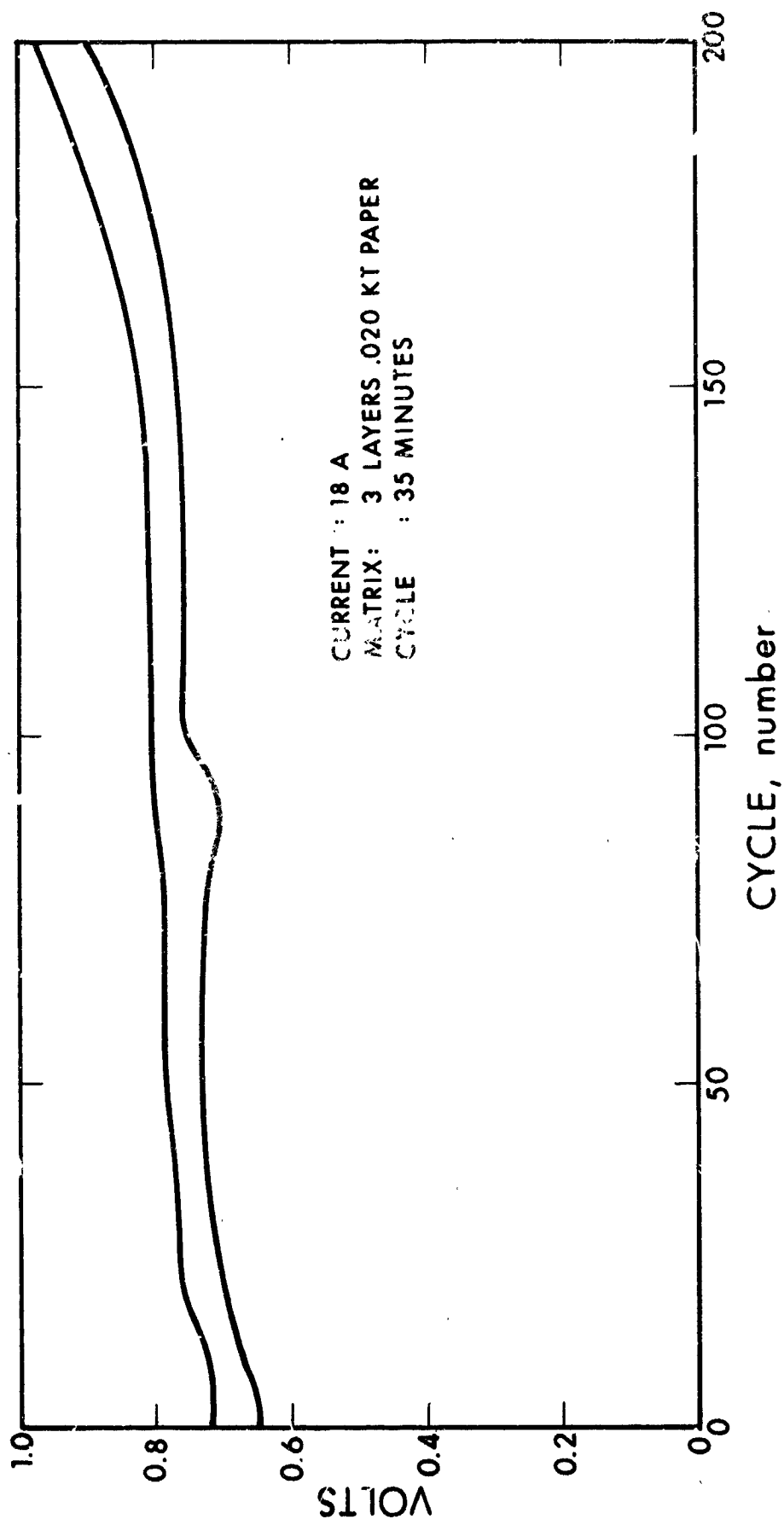


FIG. 2 CYCLING O_2 CONCENTRATION CELL 173 (midpoint voltage)

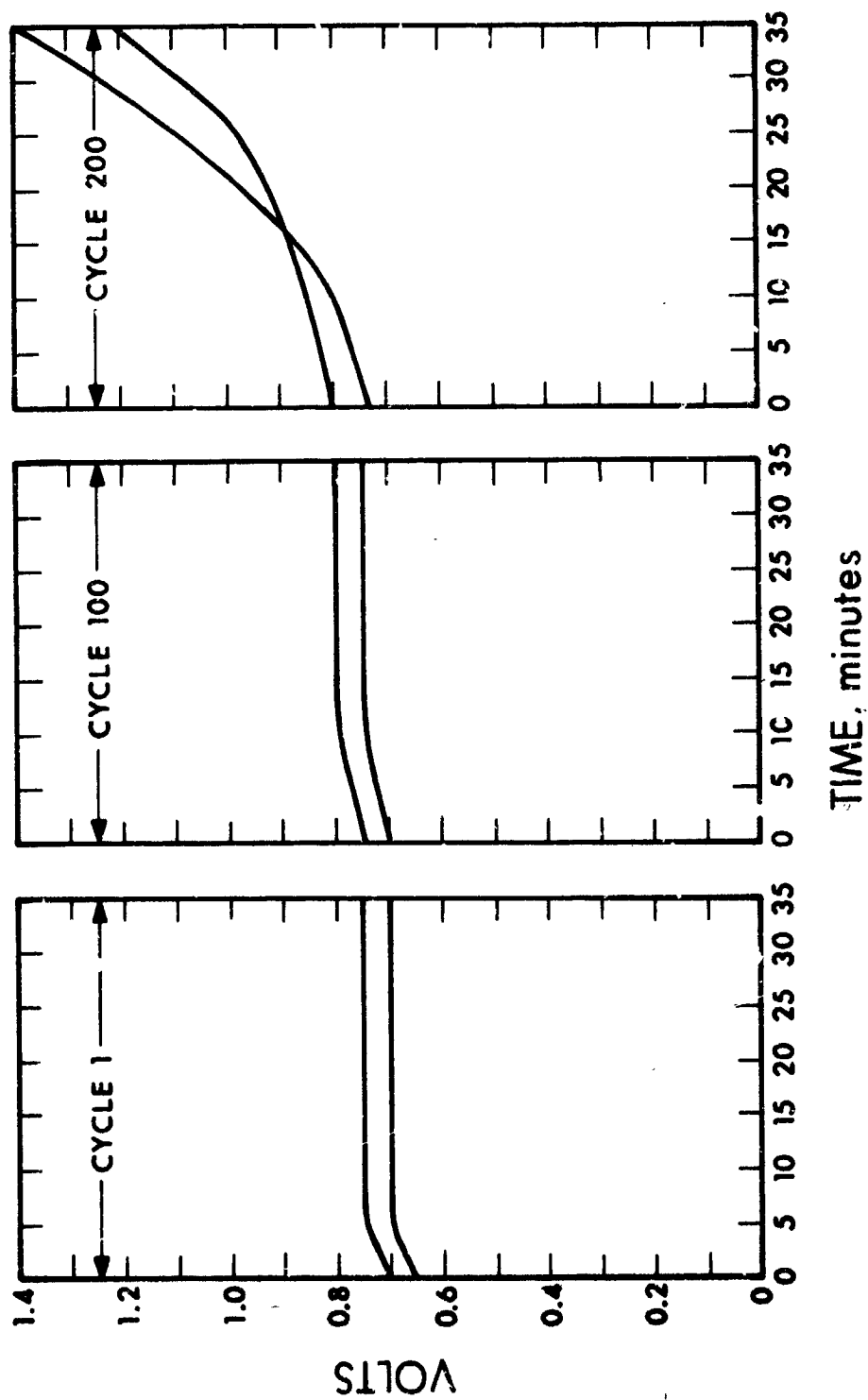


FIG. 3 CYCLING PERFORMANCE OF CELL 173

Cell No. 175 contained an oxygen electrode that was fabricated by pasting black platinum on the surface of a gold plated nickel screen. The hydrogen electrode was a standard type platinized nickel plaque. Fuel cell grade asbestos was employed as the matrix. The oxygen electrode was fabricated in an attempt to make a non-nickel substrate, non wet-proofed type of oxygen electrode. The cell was subjected to test and showed poor performance both on discharge and charge. After 10 cycles, this test was discontinued.

Cell No. 176 contained hydrogen and oxygen electrodes fabricated by the standard technique of recycling hot chloroplatinic acid through porous nickel plaques until 20 milligrams of platinum per cm^2 is deposited on the electrode. The mat consisted of four 0.020 inch layers of ACCO No. 1 asbestos manufactured by the American Cyanamid Co. Four layers of material were used to prevent possible cross leakage in the mat, since this asbestos material has a higher porosity and lower bubble through pressure than conventional fuel cell grade asbestos. The cell was subjected to cycle and exhibited low discharge voltage i.e., in a range of 0.6 to 0.7 volts. The charge voltage was good, i.e., 1.5 to 1.6 volts. The test was stopped after four cycles due to the low discharge voltage. Visual examination of the mat material showed a gray discoloration throughout the mat. An analysis of a sample of electrolyte squeezed from the mat revealed a final KOH concentration of 27.85%, indicating that this type of asbestos also reacts within the cell environment.

Cell No. 177 consisted of previously used American Cyanamid type electrodes that were acid washed in hydrochloric acid, then washed with water, soaked in potassium hydroxide and again washed with distilled water to remove any possible impurities in the electrodes. The cell was assembled with a fuel cell type asbestos mat and subjected to 3 cycles to evaluate the effect of acid washing on the electrodes. The cell exhibited good performance. At the end of three cycles, the test was discontinued to replace the fuel cell mat with an acid washed asbestos mat which was then designated Cell No. 180.

Cell No. 178 contained gold coated platinized electrodes with a fuel cell grade asbestos mat and was subjected to test in a primary mode in which gaseous oxygen and hydrogen were continuously fed to the cell. This test was conducted to determine if similar degradation would be observed in a primary mode of operation. The oxygen was dead ended and the hydrogen was allowed to vent from the cell to remove product water that was formed during discharge. For this test the standard single cell hardware that has been used in the testing of the regenerative fuel cell was utilized. In the testing of the cell, there was a gradual decrease in voltage with time. This was due to the type of construction in the cell which did not allow for intimate contact of the hydrogen gas flowing through the cell to pick up product water, and therefore the cell flooded out with time. The cell construction consists of a solid Monel back-up plate behind the electrode which contains four 1/8 inch diameter holes that allow the gas to feed to the electrode. The hydrogen gas flowing behind this back-up plate apparently did not have sufficient contact with the back side of the electrode to remove product water.

Cell No. 179 was a second attempt at a primary fuel cell using a new set of gold coated platinized electrode and fuel cell grade asbestos. In this cell the back-up plate was removed behind the hydrogen electrode and a nickel screen was put in place to facilitate water removal and intimate contact of the flowing hydrogen gas with the back surface of the hydrogen electrode. This cell, too, exhibited a gradual decrease in voltage with time, indicating improper water transport processes. These cells included 0.060 inch thick asbestos. Possibly this material reduced the transport processes as compared to 0.020 inch thick asbestos material that is normally used in primary fuel cells. Due to the water equilibration, difficulties encountered with the primary cells and a lower priority, this type test has been temporarily discontinued.

Cell No. 180 contained American Cyanamid type electrodes and a mat made from acid washed fuel cell grade asbestos. The electrodes in this cell had been previously used in Cell No. 177. The cell was cycled on a standard test cycle of 65 minutes charge, 35 minutes discharge

for 45 cycles, at which time the test was discontinued. During cycling, the charge and discharge voltage levels were good, with the exception that at the end of discharge, there would be a considerable fall-off in voltage, indicating drowning of the electrodes. Difficulties were had in getting the cell pressure above the 250 psig level, indicating that gas leakage and recombination was occurring as the mat was drying out. Due to this difficulty, the end of discharge pressure was noted to continually decrease. Analysis of a sample of electrolyte squeezed from the mat revealed a final KOH concentration of 32.9 %.

Cell No. 181 contained American Cyanamid type electrodes with a mat of three layers of 0.020 inch thick KT paper. The oxygen electrode employed was a new electrode, while the hydrogen electrode was one that had been previously used in other cell tests. The cell was subjected to test in a cycling concentration cell mode, and was tested continuously for 32 cycles. During the cycling, there was a gradual increase in voltage. The test was discontinued at the 32nd cycle when the voltage reached 1 volt.

Cell No. 182 contained porous nickel plaques that had been chemically platinized with 20 milligrams of platinum per cm² and a mat that consisted of 75 weight percent potassium titanate and 25 percent fuel cell asbestos. The potassium titanate paper used in Cells No. 173 and 181 was a sample of a material manufactured by Du Pont that has been discontinued. This material has been replaced by a pigmentary potassium titanate and is presently the only form of potassium titanate available. The new material is essentially a powder consisting of particles approximately 0.2 microns in diameter and 10 microns long. Mats for the cells fabricated from KT are made from a water slurry of the KT plus any additions desired. Forming is accomplished by filtering the slurry in a Buchner funnel. The filter cake (6-3/8" dia.) is then pressed at 10,000 pounds. Asbestos was employed within the KT material for Cell No. 182 to add additional strength to the matrix since pure "T" mats are extremely brittle. The cell was subjected to a standard test cycle, and showed good initial performance. However, during the 12th cycle, an

internal short developed in the cell. The cell was disassembled and the short traced to the outer edge of one of the electrodes. Shorting was due to an imperfection in the mat edge. Final KOH concentration of the mat was analyzed to be 35.2 %.

Cell No. 183 contained American Cyanamid type electrodes and a fuel cell grade asbestos mat that had been subjected to an acid wash process. The cell was tested in a continuous concentration cell mode and ran for a period of 140 hours to a 0.95 volt cutoff. During the period there was a gradual rise in voltage with time.

Cell No. 184 contained American Cyanamid type electrodes and an acid washed fuel cell grade asbestos mat identical in construction to Cell No. 183. This cell, too, was run in a continuous concentration cell mode and ran for a period of 72 hours to a 1.2 volt cutoff, showing a gradual rise in voltage with time. Final KOH of the cell was analyzed to be 30.5 %.

Cell No. 185 contains gold coated and platinized porous nickel plaques as the electrodes and a matrix fabricated from 75 weight percent KT and 25 percent fuel cell asbestos. The cell was subjected to test in a normal cycling manner, 65 minutes charge and 35 minutes discharge. It is presently at the 155 cycle level and is still under test. Figure 4 shows the cycling performance of this cell. There has been a gradual shifting in the performance voltage, but there has been no pattern of degradation. The differences in voltage could be attributed to variations in differential pressure and total pressure as the cell cycles. This cell exhibits a large differential swing at the initiation of charge and discharge apparently due to the oxidation of the nickel substrate. However, this performance represents the best performance achieved to date considering that > 150 cycles have been achieved and no appreciable rate of degradation observed.

Cell No. 186 contains American Cyanamid type electrodes and a mat fabricated of 75 percent KT and 25 percent fuel cell grade asbestos. This cell is being cycled in a concentration cell mode (100 ma/cm² at each polarity for 35 minutes) and has achieved 300 cycles at this time.

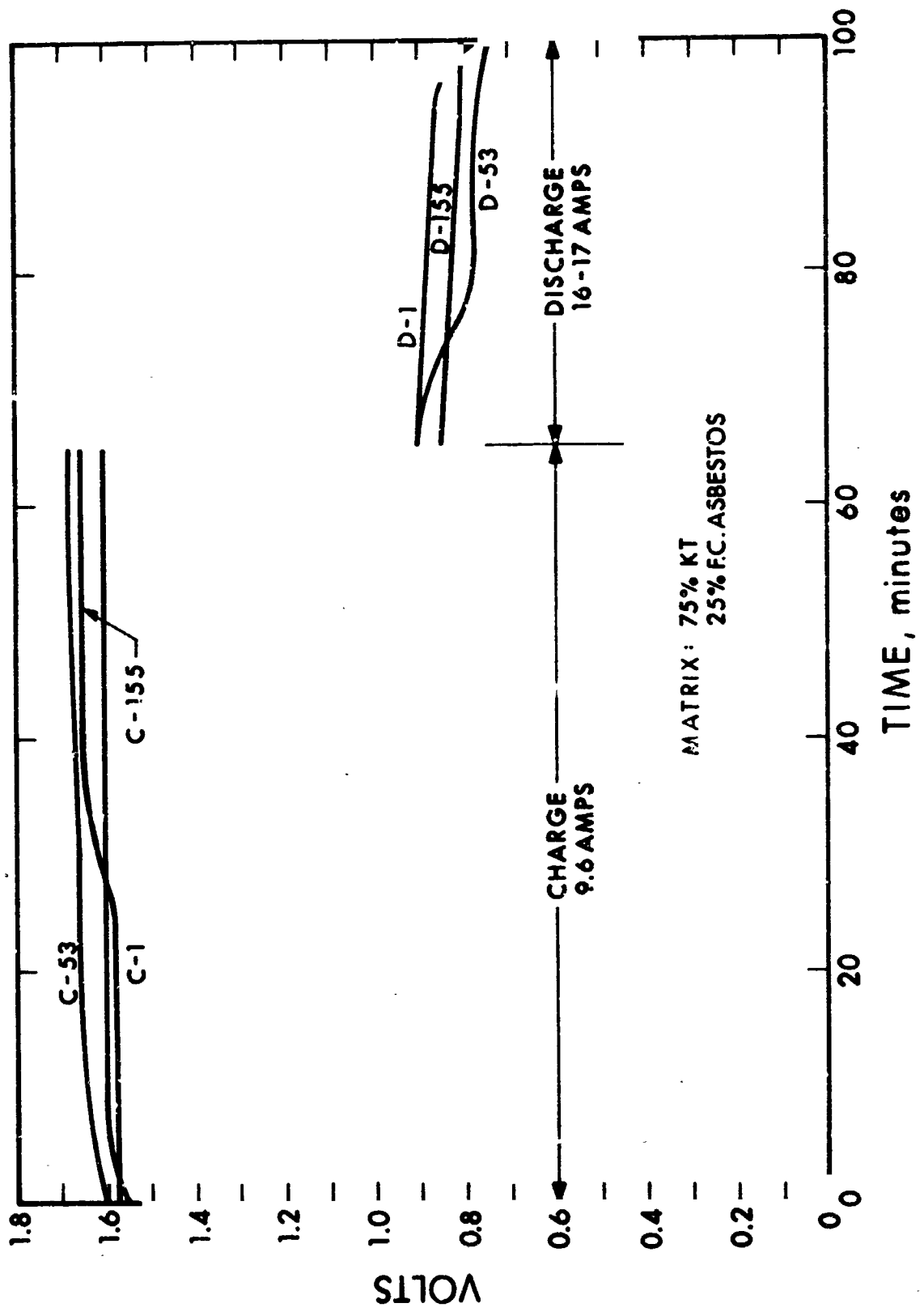


FIG. 4 CYCLING PERFORMANCE OF CELL 185

Figure 5 shows a plot of the cell voltage mid points of each cycle as a function of cycle number. As can be seen, there is a difference between the voltage of the cell as the polarity shifts. This is probably due to differences in the electrode structure. Figure 6 shows the individual voltage performance at different cycles. As can be seen, there is a gradual increase in voltage with time, but this performance is far better than any previous performance obtained and indicates a very promising solution to degradation problems encountered in the past.

Cell No. 187 contained American Cyanamid type electrodes and a matrix made of 100 % KT. This cell employed electrodes that had been previously used in a number of runs and that had possible contaminants on them. The cell ran in a test of the continuous concentration cell type for a period of 27 hours to 1.1 volt cut off. The voltage of the cell was initially high and rose rapidly to the 1.1 volt level. Analysis of the KOH concentration in the mat revealed a 35.6 %. The short run of this cell could be attributed to the old electrodes used in the cell.

Cell No. 188 also consisted of a cell employing old American Cyanamid electrodes with a 100 % KT mat in a continuous concentration cell mode. This cell, too, exhibited initial high voltage and the test was discontinued.

Cell No. 189 contained new American Cyanamid type electrodes with a 100 % potassium titanate mat. This cell developed a short in assembly and was not subjected to test.

Cell No. 190 contained the electrodes employed in Cell 189 with a matrix consisting of 100% potassium titanate. It is being subjected to a continuous concentration cell test and is still on test at this point. Figure 7 shows the voltage performance of this cell indicating a gradual rise in voltage with time.

Cell No. 191 contains a mat of 100% potassium titanate and a set of electrodes fabricated by gold coating nickel felt metal and electrodepositing 15 milligrams of platinum per cm² on the surface. This cell is under test in a continuous concentration mode, the results of which are shown in Figure 8. Performance shows a gradual climb in

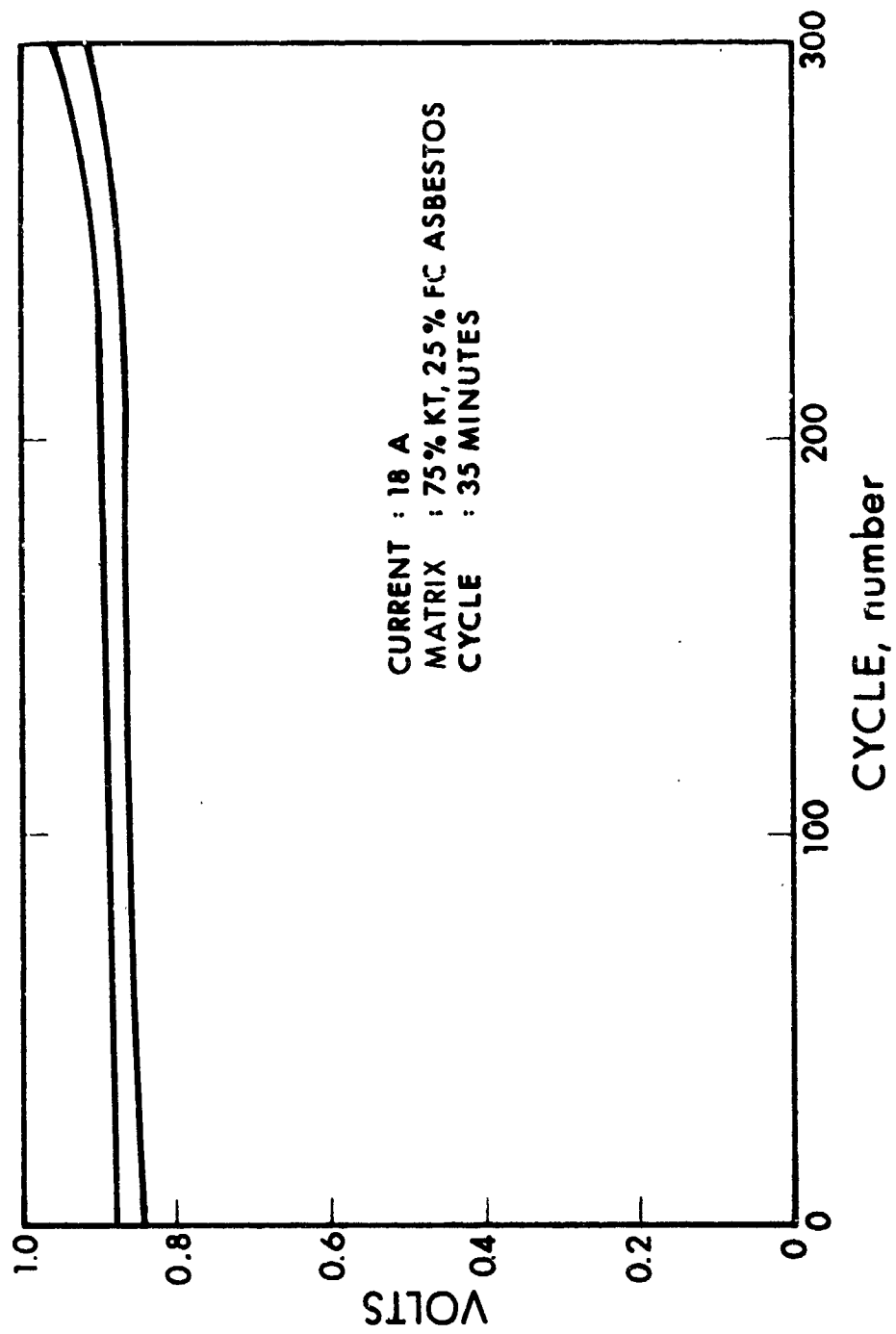


FIG. 5 CYCLING O₂ CONCENTRATION CELL 186 (midpoint voltage)

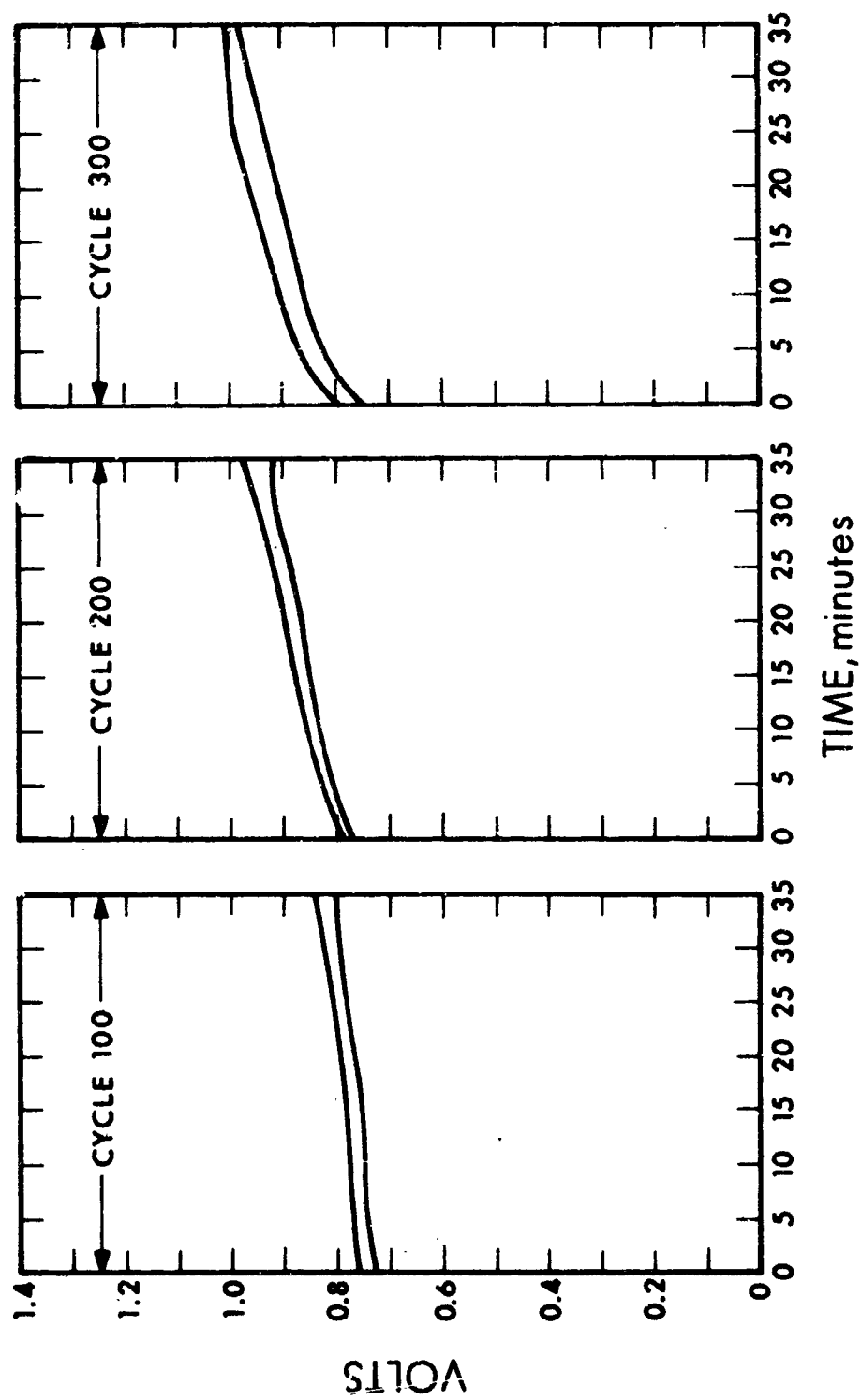


FIG. 6 CYCLING PERFORMANCE OF CELL 186

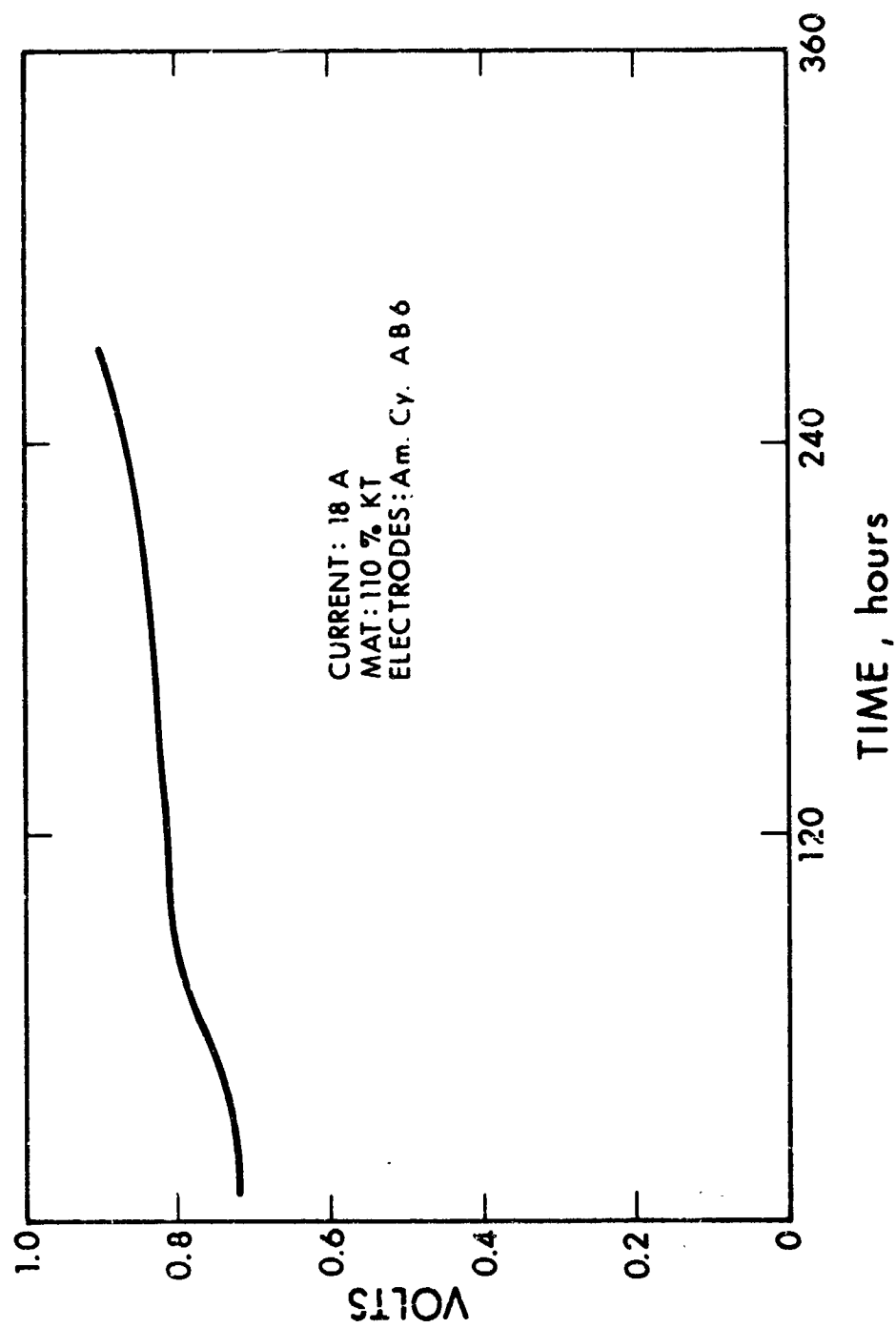


FIG. 7 CONTINUOUS O₂ CONCENTRATION CELL 190

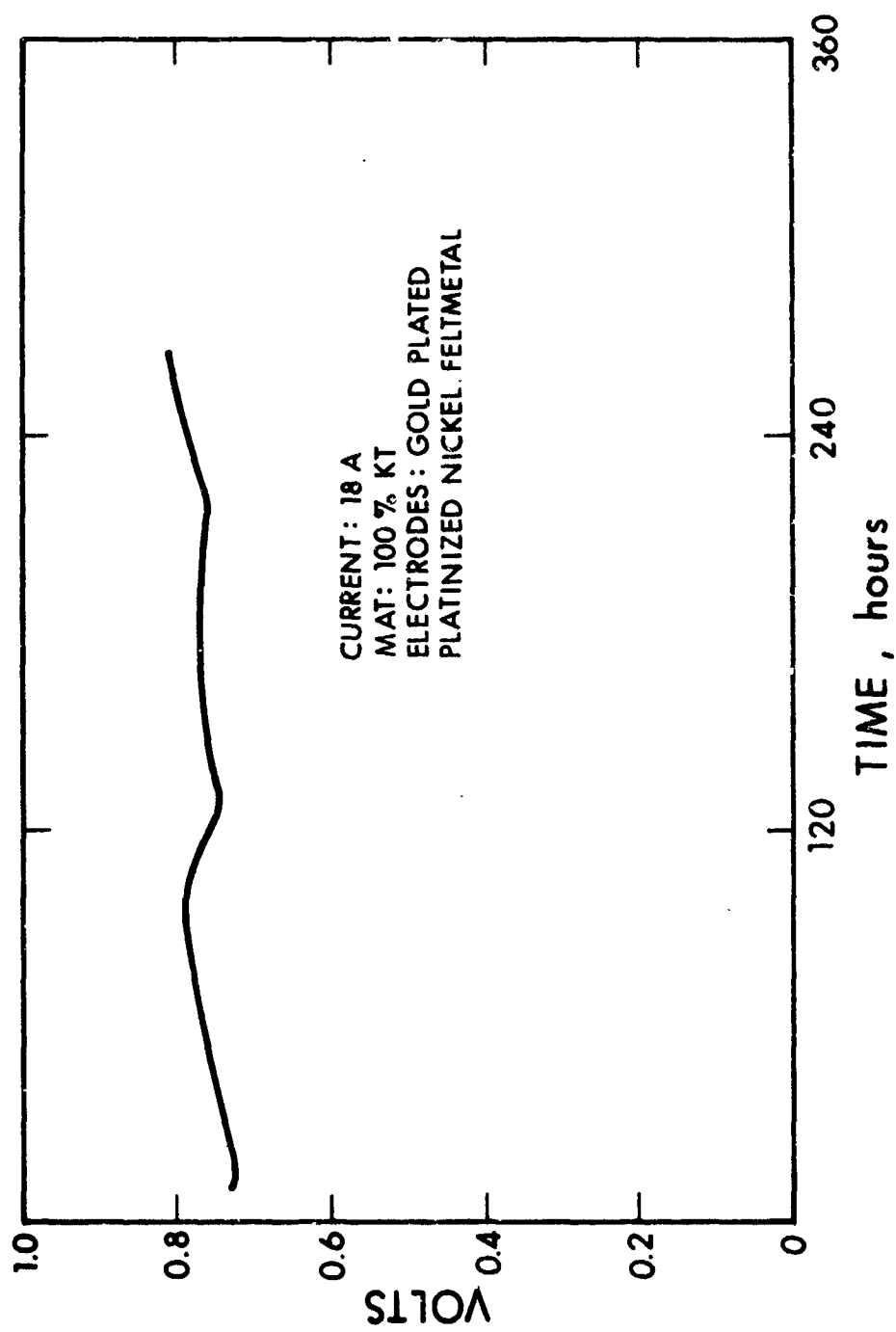


FIG. 8 CONTINUOUS O_2 CONCENTRATION CELL 191

voltage with time. The initial high point in voltage was due to a lowering of the oven temperature which was corrected. This cell is still on the test at this time. Table 2 represents a summary of all the concentration cell tests conducted thus far including cells tested in the previous report period. It shows the most recent series of cell tests employing potassium titanate are performing superior to all prior tests. The considerably improved performance of cells employing potassium titanate, either in the concentration mode or in the regular cycling mode, clearly points out that some of the prior degradations and reproducibility difficulties encountered can be attributed to the asbestos and that potassium titanate is a very promising potential solution to the difficulty. It appears to be desirable to have an additional fibrous or support constituent in the potassium titanate for mechanical strength. Several non asbestic materials such as Teflon and EP terpolymer screen or cloth are candidate constituents. The KT material also exhibits the desirable property of imbibing more water than asbestos. Its gas permeability has not been investigated in depth as yet.

2.2 Potassium Titanate Analytical Tests

To determine if any reaction occurs between potassium titanate and potassium hydroxide, tests were conducted as follows.

A 0.8454 gram sample of potassium titanate was mixed with 15 cc of 40.15 % KOH and allowed to sit for a period of 90-1/3 hours at 80°C. The titanate was then filtered from the solution, washed, dried and weighed and a weight loss of 1.67 % was obtained. An analysis of the sample of the potassium hydroxide solution, after the test period, revealed the final potassium hydroxide concentration of 40 %. Both of the changes observed could be considered within experimental error. It therefore appears that under this type of test condition, there is no appreciable reaction taking place. A second sample of 0.9954 grams of potassium titanate was mixed in a 30 grams solution of molten 70 % KOH in a platinum crucible. The solution was maintained molten for a period of 27 hours. (No temperature measurement was made during the molten period for fear of contaminating the solution, but in order for 70 %

TABLE 2

SUMMARY OF CONCENTRATION
CELL RESULTS

Cell No.	Continuous		Time to .9-1 V.	Final KOH
	Electrolyte	Matrix Type		
162	Gold coated and Pt.	F.C. Asbestos	140 hours	Reaction
167	" "	"	130 hours	29.8 %
170	" "	"	456 hours	26.25 %
183	Am. Cy.	Acid Washed Asbestos	140 hours	36.3 %
184	Am. Cy.	" "	72 hours	30.5 %
187	Am. Cy.	100 % KT	27 hours	35.6 % (Old poor electrodes)
190	Am. Cy.	100 % KT	204 ⁺ hrs.	Still on test
191	Felt metal	100 % KT	264 ⁺ hrs.	Still on test
Cycling				
163	Gold coated and pt.	F.C. Asbestos	40 hours	----
165	" "	"	152 hours	26.8 %
171	Am. Cy.	"	35 hours	28.8 %
173	Gold Coated and Pt.	Kt. (3 x .020)	224 hours	----
181	Am. Cy.	Kt. (3 x .020)	37 hours	32.9%
186	Am. Cy.	75 % Kt. 25 % Asb.	350 ⁺ hrs.	Still on test

KOH to be in a molten state, the temperature must exceed 228°C.) After the 27 hour test period, the solution was diluted and the potassium titanate filtered, washed, dried and weighed. The final weight indicated a weight loss of 5.6 % which is considered somewhat high for experimental error. In any case, the above two tests indicate that potassium titanate reacts very slowly, if at all, in a potassium hydroxide environment. Additional tests of this type will be made to establish the exact extent of reactions that may be taking place.

2.3 Multicell Testing

At the end of the last report period, as described in the 7th Quarterly Report, six cell multicell unit No. 109 was removed from testing due to poor performance. An examination of the disassembled unit revealed no obvious defects that could have caused the low performance. Analysis of the final electrolyte concentration in the asbestos mats resulted in the following:

Cell No. 1 - 27.9 %
Cell No. 2 - 27.0 %
Cell No. 3 - 23.3 %
Cell No. 4 - 23.0 %
Cell No. 5 - 26.35 %
Cell No. 6 - 28.4 %

The variation in final electrolyte concentration and the relatively low values obtained in cells No. 3 and 4 indicate the possible cause for the poor performance. These results indicate once again that the asbestos mat material was reacting with the electrolyte and probably causing the cell's poor performance.

3. PLANS FOR THE NEXT PERIOD

Single cell tests of the concentration type and fuel cell mode will be continued to evaluate potassium titanate mixtures as a matrix material. Additions of Teflon and/or asbestos will be studied to improve the physical structure of the matrices. Various electrode types including American Cyanamid, felt metal and porous carbonyl nickel plaques will be evaluated with the titanate mats. Additional analytical tests will be conducted to evaluate the extent of potassium titanate's reaction with concentrated potassium hydroxide.